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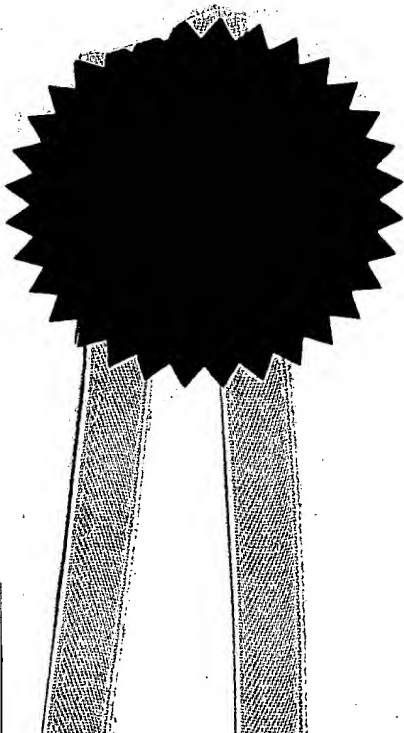
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Application for Patent

127396	מספר: Number
03-12-1998	תאריך Date
הוקדם. הדחה Ante/Post-dated	

(אני, (שם המבקש, מענו — ולגבי גוף מאוגד — מקום התאגדותו)

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כדורית לשחרור ממושך של חלבון-פוליסכריד שאינו מסיס במים ותהליך  
להכנת הנ"ל.

בעברית  
(Hebrew)

A SUSTAINED-RELEASE POLYSACCHARIDE-PROTEIN WATER INSOLUBLE  
BEAD AND A PROCESS FOR PREPARING THE SAME

(באנגלית)  
English

Hereby apply for a patent to be granted to me in respect thereof.

מבקש בזאת כי ינתן לי עליה פטנט.

<b>בקשה חלוקה</b> Application for Division	<b>בקשה פטנט מוסף</b> Application for Patent of Addition	<b>ידיעות דין קדימה</b> Priority Claim		
<b>מבקשת פטנט</b> from Application No. _____ מס' _____ Date _____ מיום _____	<b>לבקשה/לפטנט</b> to Patent/Apl. No. _____ מס' _____ Date _____ מיום _____	<b>מספר/סימן</b> Number/Mark	<b>תאריך</b> Date	<b>מדינת האירוע</b> Convention Country
<b>ייפוי כח: כללי/מיוחד — רצוף בזה / עוד יוגש</b> P. O. A.: general/specific — attached/to be filed later — Has been filed in 49011, 57024 הוגש בענין				
<b>המען למסירת הודעות ומסמכים בישראל</b> Address for Service in Israel WOLFF, BREGMAN & GOLLER P. O. Box 1352 Jerusalem, Israel, 91013				
<b>חתימת המבקש</b> Signature of Applicant WOLFF, BREGMAN & GOLLER by: <i>G. Goller</i>		היום 01 בחודש 12 שנת 1998 This of 1998		
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**A SUSTAINED-RELEASE POLYSACCHARIDE-PROTEIN WATER INSOLUBLE  
BEAD AND A PROCESS FOR PREPARING THE SAME**

כדורית לשחרור ממושך של חלבון-פוליסכריד שאינו מסיס במים ותהליך  
להכנת הנ"ל.

The present invention relates to a sustained release polysaccharide-protein bead and to a process for the preparation thereof. More particularly, the present invention relates to a sustained release polysaccharide-protein bead containing at least one volatile hydrophobic component for release therefrom in atmospheric air.

U.S. Patents 4,400,391 and 4,401,456 describe and claim alginate gel beads containing bioactive materials dispersed therein. These beads can be made to either float or sink in aqueous environments, and are capable of providing the controlled release of their bioactive materials when applied to terrestrial or aqueous environments.

The prior art deals with the controlled and/or sustained release of various materials from polysaccharide beads such as from alginate gel beads into aqueous or wet environments, however the release of hydrophobic volatile materials into the atmosphere from such a bead is neither taught nor suggested in the prior art.

With this state of the art in mind, there is now provided according to the present invention a sustained-release polysaccharide-protein water insoluble bead, comprising an emulsion of at least one protein and at least one volatile hydrophobic component contained therein, wherein said volatile component is released from said water insoluble bead in atmospheric air.

In preferred embodiments of the present invention said polysaccharide is an alginate.

In especially preferred embodiments of the present invention said protein

is gelatin.

In preferred embodiments of the present invention said polysaccharide is selected from the group consisting of carboxy methyl cellulose, chitin, pectin, chitosan and carageenan.

In preferred embodiments of the present invention said volatile component is an attractant which is preferably selected from the group consisting of eugenol, benzyl alcohol, leaf alcohols, aldehydes and acetates.

In other preferred embodiments of the present invention said volatile component is an attractant inhibitor which is preferably selected from the group consisting of (Z)-9-tetradecenyl formate and (E,E)-10,12-hexadecadienol.

In another aspect of the present invention there is now provided a process for preparing sustained-release polysaccharide-protein water insoluble beads for release of a volatile hydrophobic component therefrom in atmospheric air, comprising:

- a) preparing an oil/water emulsion by homogenizing a volatile hydrophobic component with an aqueous protein-containing solution;
- b) mixing a polysaccharide with water and adding the same to said emulsion;
- c) rehomogenizing the emulsion of step (b); and
- d) adding the emulsion step (c) in a dropwise manner into a gellant contained in an aqueous medium to form said water insoluble beads.

In preferred embodiments of the present invention said process further comprises the step of:

- e) mixing said beads with a tannin solution to effect cross-linking of the protein component of said beads, optionally followed by the further step of:
- f) drying said beads.

The beads prepared by the process of this invention are useful in providing sustained release of volatile materials contained therein, when exposed to the atmosphere. As long as the beads are kept in water, the volatile material is not released.

Said oil in water emulsion is preferably prepared by homogenization of the volatile hydrophobic component in a gelatin solution. A water-soluble salt of alginic acid is mixed with water and added to the solution. The mixture is then homogenized again, and added dropwise into an aqueous solution of di-, tri- or quatra-valent metal salt (called the gellant solution) that will cause the alginate to form gel. As each drop comes in contact with the metal salt solution, the gelation is initiated and a bead forms. Further treatment of the water-insoluble beads with tannic acid solution over night is possible if an extended delay of the release of the volatile material is desired.

More particularly, the invention describes the process and the product, which is the formulation for a slow release of pheromones.

#### DETAILED DESCRIPTION OF THE PRESENT INVENTION

In substantial similarity to U.S. 4,401, 456, the simplicity of requirements needed for carrying out the process of the present invention permits much latitude in design of equipment. A suitable apparatus, as described below, is brought only for the purpose of illustration and not to be construed as limiting the invention. The apparatus consists of a reservoir to contain the

alginate/protein/volatile- material/water emulsion that is equipped with a stopcock or similar device that allows the dropwise addition of the mixture through an orifice. The gellant solution may be contained in any convenient vessel.

After a suitable amount of time within the gellant solution, the resulting gel beads are removed by means such as filtration, screening, or straining. They may be rinsed in plain water if desired.

Beads may be further stirred in tannic acid solution and then rinsed again if a longer release-time of the volatile material is desired.

The beads can be used in this fully hydrated state or dried to any desired moisture content without losing their effectiveness. Small hard granules result when the beads are dried. The hydrophobic oil which is present within the beads, e.g. a pheromone, can be released slowly, to the atmosphere. The rate of release can be sustained by suitable selection of the concentration of the alginate, proteins, tannic acid and additional components such as polyethylene glycol, urea and electrolytes.

The rate of addition of the mixture from the reservoir is a function of orifice size and the number of orifices used. The above rate can be increased by applying air or piston pressure.

The distance between the orifice and the surface of the gellant solution should be far enough to allow the droplet to penetrate the surface of the gellant solution.

The size of the resulting alginate gel beads depends on the viscosity of the alginate/volatile material/water mixture, the amount of water retained in the beads, and orifice size. An orifice of 0.1-5 mm in diameter is suitable, but the preferred range is 0.8-2 mm. Beads will be generally spherical or ellipsoidal with an average diameter of 0.1-6 mm. Smaller beads, down to micron in size, may be prepared by spraying the alginate/volatile material/water mixture into the gellant bath.

A continuous process of producing beads is possible and requires continuous removal of gel beads and maintenance of the gellant concentration. It is also possible to extrude the alginate/volatile material/water mixture into the gellant to form a string-like gel, which can be cut into various lengths or dried and ground into granules.

Hydrated (undried) beads will usually be stored in water. The well-known phenomenon of syneresis can occur with alginate gels as well as with many other polysaccharide gels. Specifically, it is the loss of fluid (mostly water in the present invention), from the gel caused by contraction. Most of the fluid loss occurs within the 24-hour period after preparation, but it can continue for a few weeks before coming to equilibrium. Some factors that influence the amount of syneresis are alginate composition, crosslinking of the gelatin with tannic acid, temperature, gellant and the chemical nature of the volatile material. Usually the fluid that is exuded during the first 36 hours, is principally water and only a relatively small amount of volatile material is lost.

The protein used in the emulsion preparation of the present invention is a B type gelatin, but other proteins may be used as well. The concentration of the protein may vary widely and will influence the release rate of the volatile component/s.



The alginates used in the invention are any water-soluble salts of alginic acid. These include sodium, potassium, magnesium and ammonium alginate, and the alginates of organic bases such as amines. Sodium alginate is preferred. The viscosity of the alginate may vary and will influence gel strength to some degree. Highly refined alginates are not required for the practice of this invention.

An especially preferred alginate is the alginic acid, sodium salt, LX0450, available from MCB Manufacturing Chemists Inc., Cincinnati, Ohio, having a bulk density of 43 lbs./cu ft, a pH of 7.2 in a 1% aqueous solution, and a viscosity (run with a Brookfield LVF @ 60 RPM) of 400 @ 1% and 3500 @ 2%.

Concentration of the alginate formulated in the initial alginate/volatile material/water mixture is 0.1-3% by weight, but 1-1.5% is usually preferred. The volatile materials referred to in this invention are any volatile bioactive materials, such as pheromones, essential oils, pesticides, fragrances, etc.

The excellent chemical compatibility of alginates allows admixture according to the present invention with a very wide choice of volatile materials such as those described above. They are too numerous to list in their entirety. The following are only a few of the pheromones that can be used, given for the purpose of illustration and should not be construed as limiting the scope of the invention. The common name is given first, followed by the chemical name.

Common name	Chemical name
Muscamone	(Z)-9-tricosene
Gossyplure	(ZZ)-7,11-hexadecadien-1-ol acetate, and (Z,E)-7,11-hexadecadien-1-ol acetate
Disparlure	cis-7,8-epoxy-2-methyloctadecane
Grandlure	(1R-cis)-1-methyl-2-(1-methylethenyl cyclobutane)ethanol; (Z)-2-(3,3-dimethylcyclohexylidene)ethanol (Z)-(3,3-dimethylcyclohexylidene) acetaldehyde; and (E)-(3,3-dimethylcyclohexylidene) acetaldehyde

It is an important part of this invention that additional control over rate of release of these types of volatile materials may be achieved. This may be achieved by interaction between the components of the formulation with the active materials.

Concentration of the volatile material formulated in the alginate/protein/volatile material/water mixture can be as high as 50% by weight, but is preferably in the range of 0.1-20%. The ingredients of this mixture may be incorporated in any order desired prior to the emulsification process. The preferred pH range of the mixture is 4-12. The usual and preferred temperature of the mixture is 20-30°C, but may be higher to reduce viscosity.

Cations that will gel alginate solutions are the cations of barium, lead, copper, iron, strontium, cadmium, calcium, zinc, nickel, aluminum, acid ( $H^+$ ), and mixtures of these. The gellant solution of the present invention consists of an aqueous solution of a soluble and ionized salt of a metal listed above, an acid, or a mixture of these. Choice of gellant will have an effect on gel properties and possibly on the release rate of the volatile material dispersed in the alginate gel bead. The preferred gellants are the chlorides and acetates of calcium, barium and copper; the preferred acids are hydrochloric and acetic.

Concentration of the metal salt or acid in the gellant solution may be up to 50% by weight, though 1-15% is preferred. Gelation proceeds faster as the concentration is increased. Reaction with sodium alginate and certain volatile materials will reduce the effective concentration of gellant cations, therefore a sufficient concentration must be maintained to provide the desired properties.

Temperature of the gellant solution can affect gel properties. It is an advantage of the present invention, which involve volatile materials that heat does not have to be employed and most products can be made at 1-30°C. The preferred range is 20-30°C. However, any temperature up to, and including, the boiling point of the gellant solution may be used. Reaction of the alginate/volatile material/water mixture with the gellant solution is very rapid and produces a distinct gel bead immediately. Gelation proceeds from the outer surface to the center of the bead. Final gel properties such as hardness, pore size, surface area, strength, elasticity, size, durability, and release rate of the volatile material are influenced by the time within the gellant solution and should be optimized for each product. Generally, a residence time of 0.1-25 minutes may be used, but 1-10 minutes is usually sufficient.

In certain applications it may be desirable to add other ingredients to the alginate/volatile material/water mixture or to the gellant solution, or to the final gel beads. These additives may serve to alter the rate of release of the volatile material, protect the gel beads from microbial attack or oxidation, facilitate the preparation process or reduce syneresis. They include solubilizing agents, biocides such as formaldehyde, enzymes, organic solvents, surfactants, viscosity modifiers, filmforming agents, natural and synthetic gums, sequestering agents, starch, talc, fibers, light-screening chemicals and antioxidants.

Sustained release refers to formulations or materials that dispense their active ingredients into the environment over a period of time in a constant rate. For the purpose of this invention this time period can be short and measured in minutes or hours, or long and measured in days or even months. In the present invention, release of the volatile material from the alginate beads occurs through processes such as leaching, diffusion, dissolution, and degradation in atmospheric air.

Sustained release materials may be used to reduce the number of applications needed to perform a certain task, permit an effective (while not too high) concentration in the environment at any one time, and enhance effectiveness against the target species.

This invention is suitable for producing alginate gel beads containing volatile material, said beads being useful for agricultural, industrial, domestic and health-related purposes.

While the invention will now be described in connection with certain preferred embodiments in the following examples so that aspects thereof may be more fully understood and appreciated, it is not intended to limit the invention to these particular embodiments. On the contrary, it is intended to cover all alternatives, modifications and equivalents as may be included within the scope of the invention as defined by the appended claims. Thus, the following examples which include preferred embodiments will serve to illustrate the practice of this invention, it being understood that the particulars shown are by way of example and for purposes of illustrative discussion of preferred embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood

description of formulation procedures as well as of the principles and conceptual aspects of the invention.

#### EXAMPLE 1

3 grams of gelatin were dissolved in 97 grams of water. 5 grams of dodecyl acetate and 3.4 grams of water were added to 16.6 grams of the solution, and the mixture was homogenized for 5 minutes (9500 R.P.M). 2 grams of sodium alginate were dissolved in 98 grams of water, and 25 grams of the solution were added to the solution of gelatin and dodecyl acetate. The whole mixture was homogenized for 5 minutes (9500 R.P.M).

The solution was added dropwise through a syringe equipped with a 22G x 1 ½ needle, falling a distance of 60 mm, into 150 ml of 0.25%  $\text{CaCl}_2$  solution. The  $\text{CaCl}_2$  solution was contained in a 150 mm diameter vessel, and stirred with a magnetic stirrer in a rate of about 120 R.P.M. The rate of addition was such that 5 minutes were required for the 50 g addition to take place. The beads which formed (2 mm in diameter) were left in the solution for 5 additional minutes. The beads were then separated by filtration through a sieve, washed in water and stored in water. When air-dried, the beads became hard granules of about 1 mm in diameter.

#### EXAMPLE 2

Alginate beads containing dodecyl acetate were prepared as in example 1, but using  $\text{FeCl}_3$  as the gellant solution.

### EXAMPLE 3

Alginate beads containing dodecyl acetate were prepared as in example 1, but the beads formed were left over night in a 1% tannic acid solution. The beads were then washed in water and stored in water.

### EXAMPLE 4

3 grams of gelatin were dissolved in 97 grams of water. 5 grams of Gossyplure (Pink Bollworm pheromone) and 3.4 grams of water were added to 16.6 grams of the solution, and the mixture was homogenized for 5 minutes (9500 R.P.M). 2 grams of sodium alginate were dissolved in 98 grams of water, and 12.5 grams of the solution were added to the solution of gelatin and dodecyl acetate. The whole mixture was homogenized for 5 minutes (9500 R.P.M). The resulting emulsion was processed as in example 1 to produce alginate gel beads containing Gosiplure.

EXAMPLE 5

3 grams of gelatin were dissolved in 97 grams of water. 5 grams of Eugenol and 3.3 grams of water were added to 16.6 grams of the solution, and the mixture was homogenized for 5 minutes (9500 R.P.M). 3 grams of sodium alginate were dissolved in 97 grams of water, and 25 grams of the solution were added to the solution of gelatin and dodecyl acetate. The whole mixture was homogenized for 5 minutes (9500 R.P.M).

The solution was added dropwise through a syringe equipped with a 18G x 1 ½ needle, falling a distance of 500 mm, into 150 ml of 0.25%  $\text{CaCl}_2$  solution. The  $\text{CaCl}_2$  solution was contained in a 150 mm diameter vessel, and stirred with a magnetic stirrer in a rate of about 120 R.P.M. The rate of addition was such that 5 minutes were required for the 50 g addition to take place. The beads which formed (2 mm in diameter) were left in the solution for 5 additional minutes. The beads were then separated by filtration through a sieve, washed in water and left overnight in a 1% tannic acid solution. The beads were then washed and stored in water. When air-dried, the beads became hard granules of about 0.5 mm in diameter.

EXAMPLE 6

Beads were made from an emulsion of 10% Eugenol, 1% gelatin and 1.5% alginate, in the same manner described in Example 5. The beads were placed in traps that were placed in a peanut field. Together with these traps, reference traps that contained live virgin females of the beetle *Maladera Matrida* Argaman were placed in the field. After ten days, the traps containing the eugenol beads trapped as many beetles as the traps with the live females.

EXAMPLE 7

Beads were made from an emulsion of 10% pheromone of the Pink Bollworm moth, 1% gelatin and 1% alginate, in the same manner described above. The beads were placed in bags containing 200 mg of dry beads each. 25 bags were placed in a cotton field, forming a square of 50X50 meters. Reference traps containing pheromone impregnated in cardboard were placed in the middle of the square and in the field, away from the experiment. In a 90 days period, the reference traps in the field around the experiment trapped as many as 30-40 moths a day, as long as the trap in the middle of the square did not catch moths at all.

Using the beads made by Examples 1, 3, 4 and 5, the amount of volatile material released to the atmosphere was measured resulting in the amounts outlined in Table 1 "



TABLE 1:

Sample	Example	Wet Bead diameter (mm)	Dry bead diameter (mm)	Wet bead Weight (mg)	Dry bead Weight (mg)	weight of active ingredient released after 30 days (% of total)
A	1	1.5 - 2	1 - 1.5	4 - 5	1 - 2	55
B	3	1 - 1.5	1	4 - 5	1 - 2	30
C	4	1.5 - 2	1 - 1.5	4 - 5	1 - 2	50
D	5	2 - 3	0.5 - 1	5	0.5 - 1	85 (after 21 days)

The above results demonstrate that the formulations of Examples 1 and 4 have substantially similar release characteristics after 30 days. In contrast, the formulation of Example 3 (including tannic acid), exhibited a slower release rate, resulting in a lower amount of released ingredient after 30 days.

It will be evident to those skilled in the art that the invention is not limited to the details of the foregoing illustrative examples and that the present invention may be embodied in other specific forms without departing from the essential attributes thereof, and it is therefore desired that the present embodiments and examples be considered in all respects as illustrative and not restrictive, reference being made to the appended claims, rather than to the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

**WHAT IS CLAIMED IS:**

1. A sustained-release polysaccharide-protein water-insoluble bead, comprising an emulsion of at least one protein and at least one volatile hydrophobic component contained therein, wherein said volatile component is released from said water insoluble bead in atmospheric air.
2. A sustained-release polysaccharide-protein bead according to claim 1, wherein said polysaccharide is an alginate.
3. A sustained-release polysaccharide-protein bead according to claim 1, wherein said polysaccharide is selected from the group consisting of carboxy methyl cellulose, chitin, pectin, chitosan and carageenan.
4. A sustained-release polysaccharide-protein bead according to claim 1, wherein said volatile component is a bioactive material.
5. A sustained-release polysaccharide-protein bead according to claim 1, wherein said volatile component is pheromone.
6. A sustained-release polysaccharide-protein bead according to claim 5, wherein said pheromone is selected from the group consisting of grandlure, muscalure, gosiplure and disparlure.
7. A sustained-release polysaccharide-protein bead according to claim 1, wherein said volatile component is an essential oil.
8. A sustained-release polysaccharide-protein bead according to claim 1, wherein said volatile component is a pesticide.

9. A sustained-release polysaccharide-protein bead according to claim 1, wherein said volatile component is an attractant.
10. A sustained-release polysaccharide-protein bead according to claim 9, wherein said attractant is selected from the group consisting of eugenol, benzyl alcohol, leaf alcohols, aldehydes and acetates.
11. A sustained-release polysaccharide-protein bead according to claim 1, wherein said volatile component is an attractant inhibitor.
12. A sustained-release polysaccharide-protein bead according to claim 11, wherein said attractant inhibitor is selected from the group consisting of (Z)-9-tetradecenyl formate and (E,E)-10,12-hexadecadienol.
13. A sustained-release polysaccharide-protein bead according to claim 1, wherein said volatile component is present in an amount of up to 50% wt./wt.
14. A sustained-release polysaccharide-protein bead according to claim 1, wherein said volatile component is present in an amount of up to 20% wt./wt.
15. A sustained-release polysaccharide-protein bead according to claim 1, wherein said protein is a gelatin.
16. A sustained-release polysaccharide-protein bead according to claim 15, wherein said gelatin is a type B gelatin.
17. A sustained-release polysaccharide-protein bead according to claim 1, wherein said volatile component is Eugenol.

18. A sustained-release polysaccharide-protein bead according to claim 1, further comprising tannic acid for effecting a slower release rate.

19. A process for preparing sustained-release polysaccharide-protein water insoluble beads for release of a volatile hydrophobic component therefrom in atmospheric air, comprising:

a) preparing an oil/water emulsion by homogenizing a volatile hydrophobic component with an aqueous protein-containing solution;

b) mixing a polysaccharide with water and adding the same to said emulsion;

c) rehomogenizing the emulsion of step (b); and

d) adding the emulsion of step (c) in a dropwise manner into a gellant contained in an aqueous medium to form said water insoluble beads.

20. A process according to claim 19, further comprising the step of:

e) mixing said beads with a tannin solution to effect cross-linking of the protein component of said water insoluble beads.

21. A process according to claim 20, further comprising the step of:

f) drying said beads.

22. A process according to claim 19, wherein said polysaccharide is an alginate.

23. A process according to claim 19, wherein said polysaccharide is selected from the group consisting of carboxy methyl cellulose, chitin, pectin, chitosan and carageenan.

24. A process according to claim 19, wherein said volatile component is a bioactive material.
25. A process according to claim 19, wherein said volatile component is pheromone.
26. A process according to claim 25, wherein said pheromone is selected from the group consisting of grandlure, muscalure, gosiplure and disparlure.
27. A process according to claim 19, wherein said volatile component is an essential oil.
28. A process according to claim 19, wherein said volatile component is a pesticide.
29. A process according to claim 19, wherein said volatile component is an attractant.
30. A process according to claim 29, wherein said attractant is selected from the group consisting of eugenol, benzyl alcohol, leaf alcohols, aldehydes and acetates.
31. A process according to claim 19, wherein said volatile component is an attractant inhibitor.
32. A process according to claim 31, wherein said attractant inhibitor is selected from the group consisting of (Z)-9-tetradecenyl formate and (E,E)-10,12-hexadecadienol.

33. A process according to claim 19, wherein said volatile component is present in an amount of up to 50% wt./wt.
34. A process according to claim 19, wherein said volatile component is present in an amount of up to 20% wt./wt.
35. A process according to claim 19, wherein said protein is a gelatin.
36. A process according to claim 35, wherein said gelatin is a type B gelatin.
37. A process according to claim 22, wherein said alginate is a water-soluble salt of alginic acid.
38. A process according to claim 22, wherein said alginate is a water-soluble salt of organic bases.
39. A process according to claim 22, wherein said alginate is selected from the group consisting of sodium, potassium, magnesium, ammonium alginate and amines.
40. A process according to claim 22, wherein said alginate is present in an amount of about 0.1-5% wt./wt.
44. A process according to claim 22, wherein said alginate is present in an amount of about 1-1.5% wt./wt.
42. A process according to claim 19, wherein said gellant is an aqueous metal salt solution.


43. A process according to claim 42, wherein said aqueous metal salt solution comprises a divalent or trivalent metal salt.

44. A process according to claim 42, wherein said metal salt solution comprises chlorides and acetates of calcium, barium and copper.

45. A process according to claim 19, wherein the emulsion of step (c) is sprayed into said gellant to form micron-sized beads.

For the Applicant

**WOLFF, BREGMAN AND GOLLER**

by: 

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